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SUBJECT—

TITLE

WATER EMULSIONS FOR PENETRATING SPRAYS

~~1943~~

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Memorandum for the files concerning:

Laboratory Tests to Develop a Stable Emulsion
1943

Reason for Tests

Control of the mountain pine beetle by use of oil-base orthodichlorobenzene sprays has proved quite feasible both in lodgepole and western white pine. An objectionable feature, however, has been the necessity for and attendant high cost of transporting oil and lethal agent to place of use. It was thought the substitution of water for oil as the carrier of the lethal agent would decidedly reduce spray costs if it could be used. With these two objectives in view, experiments have been conducted to develop a spray that is easy to mix, stable in character, and lethal in effect.

Previous Tests

In previous experience with emulsions some reactions, surprising to the writer, were noted. In adding water slowly to mixtures of emulsifiers and lethal agent while vigorously stirring them, the entire liquid would suddenly "set" to the consistency of a thick custard. Laborious stirring, while adding the remainder of the necessary water ratio, was necessary over a long period before the lumps could be stirred out of the mixture. Because mixing directions had been followed closely, it was felt that that phase was not at fault but that some other factor was affecting results. It was decided to try rapid mixing instead of the recommended slow method. This was to be accomplished by pouring the required amount of water into the previously well-mixed emulsifiers and lethal agent, from a height of about four feet, repeating that action as many as fifty times, between two receptacles. This was done, found to prevent "setting" of the mixture, and proved decidedly time-saving. Believing, from the preceding experiences, that either manner or order of mixing ingredients, as well as the kind and amount of them, might decidedly affect the resulting emulsion, a series of experiments were initiated centered around the first two variables. They were as follows:

Mixing variations

(1) Stirring vigorously while slowly adding water to the mixture of the other three ingredients

(2) Rotating previously mixed ingredients in container while slowly adding water, followed by vigorous stirring

(3) Rapid mixing, by pouring water quickly into three already mixed ingredients, then continuing pourings between two receptacles for a total of fifty times

(4) Pouring water into three mixed ingredients, then mixing by 200 turns of an egg beater rotated at uniform high speed.

For more ready observation of rate and amount of settling, the emulsions were placed in long slim glass tubes.

The results of these tests fell into two general classes, in the first of which the emulsified material concentrated or settled in the lower part of the tube and in the second the separation of opaque material was toward the top, with increasingly clear liquid toward the bottom of the tube. Inverting into alternate receptacles and mixing by means of an egg beater produced the first class; either stirring or rotating the mixture during the slow addition of water, or combining both methods, produced the second class. The results seemed to be distinctive because a number of remxings of those in the second class by the methods used in the first, failed to change the manner of subsequent separation. This indicates two kinds of emulsions with distinctive physical and possibly chemical, differences. Tabulation of the data from the first of these experiments is presented in Table 1, on the following page.

None of the tests presented in Table 1 met the arbitrary requirements of remaining emulsified for at least 24 hours. Doubling the quantity of triethanolamine not only failed to increase the stability of the emulsion but seemed to favor an even more rapid breakdown.

Order of mixing of ingredients made no apparent difference even when water was added to the oleic acid and triethanolamine prior to the orthodichlorobenzene.

Varying the quantity of ingredients

In another series of nine experiments the quantity of orthene[1] was kept constant but the amount of water and other ingredients was varied. All mixing in these experiments was done with an egg beater operated at a uniformly high speed for 200 turns, unless otherwise noted. The data from these experiments are shown in Table 2.

Table 2 - Tests to Develop a Stable Emulsion - 1943

Exp. no.	c. c. of ingredients: Water	Orthene	Oleic acid	Triethanolamine	Results
2	100	25	5.0	2.0	Remained emulsified overnight and readily returned to emulsion after some "settling out".
3	150	25	5.0	2.0	Same as for preceding experiment.
4	200	25	5.0	2.0	Unsatisfactory
5	100	25	1.25	.5	"
6	150	25	1.25	.5	"
7	200	25	1.25	.5	"
8	100	25	2.5	1.0	"
9	150	25	2.5	1.0	"
10	200	25	2,5	1.0	Separates too rapidly, but little action necessary to restore to emulsified condition.

(1) Abbreviation of orthodichlorobenzene

Table 1 — Effects of Manner and Order of Mixing on Emulsion Characteristics — 1943

Experiment 1

Test number	Cubic centimeters of ingredients and mixing order: Water	Orthodichlorobenzene	Oleic acid	Triethanolamine	Manner of mixing	Condition of emulsion column 24 hours after mixing at its: Base	Middle	Top
1	95 4	31.5 3	4.0 2	1.5 1	Stirred initially-(1) remixed 24 hrs. later by 50 pourings between two receptacles	5/8" clear liquid	8" like clabber	
2	4	3	2	1	Poured between two receptacles 50 times, followed by stirring	5¼" like clabber	3" partly clear	½" clear
3	4	3	2	1	Rotated in receptacle, followed by stirring	1¼" clear	8" like clabber	
4	3	4	2	1	Stirred, followed 24 hrs. later by 50 pourings between 2 receptacles	1" clear	8" like clabber	
5	3	4	2	1	Stirred long and vigorously	1 1/8" clear	8" like clabber	
6	4	3	2	1	Stirred long and vigorously	1" clear	8" like clabber	
7	4	3	2	1	Poured between 2 receptacles 50 times	5½" like thin custard	2 3/4" cloudy	½" clear
8(2)	4	3	2	1	Poured between two receptacles 50 times	1½" like custard	7" like thin custard	
9	4	3	2	1	Egg beater rotated 200 times	4 3/8" like custard	1 1/8" cloudy	¼" clear
10	95	31.5	4.0	3.0	Egg beater rotated 200 times	2 3/8" orthene layer	2 7/8" like thin custard	1/8" clear

(1) With glass stirring rod (2) Light green dye added to aid in identifying layering

To more accurately determine the stability of the emulsions, a slit was cut in the side of a corrugated board carton. Immediately above the slit, a hole was cut in the top of the box, large enough to insert the test tubes being used and to hold them against the slot. A 100-watt frosted light in the box, so placed that the tube in the slot was between the light and the observer, revealed separation of the contents of the tube long before it could have been detected without such an aid.

In mixing the spray ingredients, it was found that rotating the egg beater at high speed usually caused a quick change from a liquid to a whipped cream consistency of many of the emulsions. In general this occurred after at least 100 turns of the egg beater, with about 150 turns being the average. Emulsions brought to that stage separated much more slowly than those which did not reach the whipped cream consistency.

Although the results from some of Experiments 2 to 10 were quite encouraging, none of the mixtures were considered sufficiently stable.

Two groups of experiments were then planned, in the first of which the amount of water, orthene, and oleic acid was kept constant, but the quantity of triethanolamine was varied. In the second group, the amount of oleic acid was varied. The data from these two groups are presented in Table 3.

Table 3 - Tests to Develop a Stable Emulsion - 1943

Exp. no.	c. c. of Ingredients: Water	Orthene	Oleic acid	Triethanolamine	Final results
					Group 1
11	100	25	2.5	1.5	Not acceptable but showing promise because of slowness in stratification and rapid return to emulsion when but gently remixed.
12	100	25	2.5	2.0	Two tests gave results quite similar to those of Experiment 11.
13	100	25	2.5	2.5	Same results as for preceding two experiments.
14	100	25	2.5	3.0	Unsatisfactory.
15	100	25	2.5	3.5	Unsatisfactory.
					Group 2
16	100	25	2.0	2.0	Unsatisfactory.
17	100	25	1.5	2.0	Unsatisfactory.
18	100	25	1.0	2.0	Same general results as for experiments 11 to 13 but after 9 days experiments 12 and 18 showed slowest separation of emulsions.
19	100	25	.5	2.0	Unsatisfactory.
20	100	25	none	2.0	Unsatisfactory.

Six of the preceding ten experiments gave promising results, as indicated by slow stratification of the emulsion. Also, very little action was necessary to restore the emulsions to an apparently thoroughly mixed condition. The preceding characteristics would be of decided value on a control project where partly-filled spray tanks might have to be left overnight at place of use and ease of remixing the following day would be an important advantage.
The promising results from six of the preceding ten experiments, formed the basis for a series of seven more experiments in which both oleic acid and triethanolamine were varied but the amount of water and orthene was kept constant. The data for these seven experiments are given in Table 4.

Table 4 - Tests to Develop a Stable Emulsion - 1943

Exp. no.	C. c. of Ingredients Water	Orthene	Oleic acid	Triethanolamine	Final results
21	80	20	2.0	.8	Unsatisfactory.
22	80	20	1.5	.6	Unsatisfactory.
23	80	20	1.0	.4	Unsatisfactory.
24	80	20	.5	.2	Unsatisfactory.
25	80	20	2.5	1.0	Unsatisfactory.
26	80	20	3.0	1.2	Unsatisfactory.
27	80	20	3.5	1.4	Unsatisfactory.

None of the preceding seven experiments gave even promising reactions. Separation of the emulsion was too rapid.
Two experiments were initiated with the miscible orthene sent from the Morristown, New Jersey Laboratory, for comparison with those developed at the Coeur d'Alene Laboratory. One experiment included the supplied wetting agent, the other did not. In both cases the other ingredients were in proportions suggested by the Morristown Laboratory. The emulsion without wetting agent was mixed by 100 turns of the egg beater, one-half the number given other tests, while that with wetting agent was merely stirred with a glass rod. Both mixtures showed equally excellent stability.
The possibility that another wetting agent might be more effective than those already tested led to the initiation of experiments using Triton 720 alone and in combination with oleic acid. These experiments are listed in Table 5.

Table 5 - Tests to Develop a Stable Emulsion - 1943

Exp. no.	C. c. of Ingredients: Water	Orthodene	Oleic acid	Triton 720	Final results
30	80	20	-	1	Unsatisfactory.
31	80	20	-	2	Unsatisfactory.
32	80	20	-	4	Unsatisfactory.
33	80	20	-	8	Unsatisfactory.
34	80	20	-	12	Unsatisfactory.
35	80	20	.5	1	Unsatisfactory.
36	80	20	1.0	1	Unsatisfactory.
37	80	20	1.5	1	Unsatisfactory.
38	80	20	2.0	1	Unsatisfactory.

None of these tests gave even promising results. Sedimentation was too rapid. Many of these emulsions foamed to a high degree during the 200 turns of the egg beater. In previous experiments foaming had usually been an indication of a stable emulsion but did not prove so in these tests. They showed rapid separation of ingredients.

References in Shepard's "The Chemistry and Toxicology of Insecticides" to the use of phenols in emulsions prompted experiments with that as an ingredient of the emulsions. Six experiments were run, with phenol a constant ingredient in five of them and the oleic acid and triethanolamine varied in amount. Chemically-pure phenol crystals were dissolved by slow heating to secure the indicated amount of that ingredient. The data are given in Table 6.

Table 6 - Tests to Develop a Stable Emulsion - 1943

Exp. no.	Cubic Centimeters of Ingredients: Water	Orthene	Oleic acid	Triethanolamine	Phenol	Final results
39-1	80	20	2.5	1.0	1.0	Promising; settled out quite slowly.
2	80	20	2.5	1.0	1.0	Replicate. Differed slightly in appearance but gave same promising results as indicated by slow settling.
3	80	20	2.5	1.0	none	Unsatisfactory.
40	80	20	2.0	.8	1.0	Unsatisfactory.
41	80	20	1.0	.4	1.0	Unsatisfactory.
42	80	20	1.0	.8	1.0	Unsatisfactory.

Promising results with Experiment 39-1 led to the replication (39-2) and variation (39-3) of it, omitting only the phenol. Tests 1 and 2 of Experiment 39 indicated a slow-settling emulsion. Without phenol the emulsion settled quite rapidly. The other experiments were unsatisfactory in that the emulsions broke down rapidly.
Triton 720 had been tested with oleic acid as an emulsifying aid and been found unsatisfactory in the associations tested. Possibility of more favorable results with triethanolamine led to tests in combination of it with Triton 720, orthene and water being held constant in amount and the triethanolamine varied. The data of these four tests are given in Table 7.

Table 7 - Tests to Develop a Stable Emulsion - 1943

Exp. no.	C. c. of Ingredients: Water	Orthene	Triton 720	Triethanolamine	Final results
43	80	20	1.0	.5	Unsatisfactory.
44	80	20	1.0	1.0	Unsatisfactory.
45	80	20	1.0	2.0	Unsatisfactory.
46	80	20	1.0	4.0	Unsatisfactory.

Rapid stratification indicated the instability of these emulsions. Encouraging results with Experiment 39 prompted further experimentation based on the same proportions of the various ingredients. Experiments 47

to 51 and their replicates are given in Table 8.

Table 8 - Tests to Develop a Stable Emulsion - 1943

Exp. no.	Cubic centimeters of Ingredients: Water	Orthene	Oleic acid	Phenol	Triethanolamine	Results
47-1	80	20	2.5	1.0	1.5	Excellent
2	80	20	2.5	1.0	1.5	Excellent
3	80	20	2.5	1.0	1.5	Excellent
4	80	20	2,5	1.0	1.5	Excellent
48	80	20	2.5	1.0	2.0	Unsatisfactory- settles too rapidly.
49	80	20	2.5	1.0	2.5	Same results as for Experiment 48.
50	80	20	2.0	1.0	2.0	Good, but settles out more rapidly than Experiment 47.
51-1	80	20	1.5	1.0	1.5	Very good
2	80	20	1.5	1.0	1.5	Not as good as 51-1 but still acceptable
3	80	20	1.5	1.0	1.5	Same as 51-2
4	80	20	1.5	1.0	1.5	Excellent
5	80	20	1.5	1.0	1.5	Not as good as 51-1 or 4
6	80	20	1.5	1.0	1.5	Excellent
7	80	20	1.5	1.0	1.5	Not as good as 51-1, 4 or 6

All four tests of Experiment 47 gave satisfactory results. There were slight differences in the period required for the emulsions to "settle out" but all met the arbitrary requirements of remaining adequately mixed for at least 24 hours.

Experiments 48 and 49 were unsatisfactory because of the rapid "settling out" of the emulsion. These two experiments varied only from Experiment 47 in larger amounts of triethanolamine. That amount, however, was apparently sufficient to upset the delicate balance of the emulsions and cause their breakdown.

In Experiment 50, changes in the amount of oleic acid and phenol resulted in a less stable emulsion than in Experiment 47 but gave results that are

acceptable but inferior to those obtained in other experiments.
Some of the seven replicates of Experiment 51 gave excellent results, others were not so good. The reason for these differences is not apparent.
Test 4 was initially mixed by only ten turns of the egg beater. This was insufficient as was indicated by the readiness with which the mixture separated. However, remixing by 200 turns of the egg beater produced an acceptably stable emulsion. Test 6 also gave excellent results.
Experiments were initiated in which the water, orthene, and triethanolamine were kept constant and the oleic acid and phenol were varied in amount. The seven experiments are shown in Table 9.

Table 9 - Tests to Develop Emulsion - 1943

Exp. no.	C. c. of Ingr. Water	Orthene	Oleic Acid	Phenol	Triethanolamine	Results
52			2.5	1.5		Unsatisfactory
53			2.0	1.5		Unsatisfactory
54	80		1.0	2.5	1.5	Unsatisfactory
55	80	20	1.5	2.0	1.5	Unsatisfactory
56	80	20	2.0	1.25	1.5	Unsatisfactory
57	80	20	2.0	1.0	1.5	Acceptable - remained emulsified for about 36 hours
58	80	20	1.5	.5	1.5	Unsatisfactory

Only one of the series shown in Table 9 gave promising results, Experiment 57, which remained stable for about 36 hours. However, as other experiments have given even better results, they are to be preferred.
Three experiments were run with creolin in place of the phenol. At the same time four additional experiments were run with phenol and Triton 720 as the emulsifying agents. The seven experiments are shown in Table 10, shown on page 10.

Although Experiments 59 and 64 gave promising results, they were insufficiently so to be acceptable. However, the promising results from Experiment 59 prompted further experimentation around that formula as a base. These two sets of experiments are shown in Table 11.

Table 10 - Tests to Develop a Stable Emulsion - 1943

Exp. no.	Cubic centimeters of Ingredients: Water	Orthene	Cleic acid	Creolin	Triton Tr720	Triethanolamine	Results
59	80	20	2.5	1.0	-	1.5	Promising-slow to separate
60	80	20	2.0	1.0	-	1.5	Unsatisfactory
61	80	20	1.5	1.0	-	1.5	Unsatisfactory
				Phenol			
62	80	20	-	1.0	-	1.0	Unsatisfactory
63	80	20	-	1.0	-	2.0	Unsatisfactory
64	80	20	-	1.0	-	3.0	Promising-slow to separate
65	80	20	-	2.0	-	1.0	Unsatisfactory

Table 11 - Tests to Develop a Stable Emulsion - 1943

Exp. no.	C. c. of Ingredients: Water	Orthene	Cleic acid	Creolin	Triethanolamine	Results
66	80	20	3.0	1.0	1.5	Unsatisfactory
67	80	20	2.5	1.0	1.5	Unsatisfactory
68-1	80	20	2.5	1.5	1.5	Unsatisfactory
2	80	20	2.5	1.5	1.5	The addition of 1.0 c.c. of absolute ethyl alcohol failed to improve results
3	80	20	2.5	1.5	1.5	Unsatisfactory
69-1	80	20	2.5	.5	1.5	Acceptable
2	80	20	2.5	.5	1.5	Acceptable- differed only in the manner of mixing from 69-1. Results similar
			Triton 720	Phenol		
70	80	20	3.5	1.0	--	Acceptable
71	80	20	4.0	1.0	--	Unsatisfactory

Experiment 70 and the two tests of experiment 69 gave acceptable results but other even more satisfactory emulsions place these experiments in a secondary position.

Conclusions and summary

From the experiments conducted it was found that the order in which emulsion ingredients were mixed had no apparent influence on the physical properties of the emulsion. However, manner of mixing did seem to greatly influence results. The thorough mixing accomplished by use of an egg beater resulted in a much more stable emulsion than was obtained by the less vigorous stirring method, by rotating the container, or by pouring from one receptacle to another. The use of the egg beater produced a whipped cream effect which seemed to greatly increase the stability of the emulsion. Rapid mixing, as secured by pouring the ingredients from one receptacle to another, or by the use of the egg beater, also seemed to prevent the "setting" of mixtures at a certain point in the addition of water. This "setting" which was noted with gradual addition of water to spray ingredients, necessitates the slow and laborious stirring of the mixture while the remainder of the required water is being added, in order to obtain a uniform consistency of the emulsion.
Quite a number of the experiments gave acceptable results. Eleven met the arbitrary requirements of remaining in an emulsified state for a minimum of 24 hours or had other compensating properties. Some of them gave better results than others. Those which gave acceptable or better results are presented in Table 12.

Table 12 - Experiments Which Have Given Favorable Results in Seeking to Develop a Stable Emulsion
1943

Exp. no.	Cubic centimeters of Ingredients: Water	Orthophene	Oleic acid	Creolin	Phenol	Triethanolamine	Results
12	100	25	2.5	-	-	2.5	Emulsion separates slowly
18	100	25	1.0	-	-	2.0	Same as for Experiment 12
39	80	20	2.5	-	1.0	1.0	Emulsion separates slowly
47	80	20	2.5	-	1.0	1.5	Excellent stability in all four tests
50	80	20	2.0	-	1.0	2.0	Not quite as stable as Experiment 47
51	80	20	1.5	-	1.0	1.5	Some excellent results in the seven tests but variability noted
57	80	20	2.0	-	1.0	1.5	Remained stable for 36 hours
59	80	20	2.5	1.0	-	1.5	Slow separation of emulsion
64	80	20	-	1.0	-	3.0	Slow separation of emulsion
69	80	20	2.5	.5	-	1.5	Slow separation of emulsion in the two tests
70	80	20	4.0	1.0	-	-	Acceptable, but not as good as some of the others

While the evidence must not be considered conclusive, because of the small amount of testing of each emulsifier or combination of them, those containing phenol seemed to be the most stable. Although the preceding experiments have revealed a number of emulsions of satisfactory stability, none were tested for lethal properties to bark beetles or for bark-penetrating qualities. Limited time and press of other work made it impossible to conduct such tests, on any but a very limited scale. For that reason it was decided to limit field experiments to emulsions which had shown promising lethal qualities in the past, adding to them the ingredient phenol. Results of these field tests were unsatisfactory in that the results were too variable to be acceptable. Results of these tests were reported earlier in the year.(1)

If at some future time it is decided that further tests with emulsions to control bark beetles are advisable, it is felt that the more promising of these formulae will serve as a background for such work.

(1) " Tests of Penetrating Sprays to Control the Mountain Pine Beetle in Western White Pine" By A.L. Gibson, Feb. 22, 1944. Report of the Forest Insect Laboratory at Coeur d'Alene, Idaho.